

182°C. The millings were then followed with a White clean-up mill sheet compound according to industry standards. The samples were then ranked according to relative out resistance. For compatibility testing, milled stock was cut into strips and aged for 30 days at 71°C and 100% relative humidity. Samples were then ranked according to relative color retention and tendency to spew. For relative clarity, 1/8" (0.32 cm) plaques were pressed at 190°C for 2 minutes, then compared against a printed background for relative crispness of letters through the plaques. For stabilizer volatility, a percentage weight loss was measured as a difference between the start and end weight of the stabilizer samples as measured in an oven after two (2) hours at 110°C.

Example #1

Four stabilized flexible PVC resin formulations (two Prior Art, i.e., compositions V and W as well as two of the instant invention, i.e., compositions B and C) were made in accordance with the components and quantities thereof as shown in Table III.

Table III

Component	<u>Parts</u>
PVC Resin	100
Plasticizer	40
Epoxidized soybean oil	5
Stabilizing blend	3

The Yellowness Index was measured for two prior art stabilizer additive packages in contrast to two compositions of the instant invention in Table IV in a short term static heat stability test. As is clearly seen in the table, the heat stability was not only equivalent to, but superior to Prior Art formulations, but without additional heavy metals. Equally significant to the fact that the heavy metal of Ba in the case of Prior Art formulation V and of Ba and Cd in the case of Prior Art formulation W, were eliminated in the formulations of the invention, but additionally resulted in superior clarity, a highly desirable feature in PVC signage.

Table IV

Color (Yellowness Index) Value				
Time (min)	Prior Art V	Prior Art W	B (150 ppm Zn)	C (180 ppm Zn)
0	2.9	2.4	1.3	1.6
30	6.1	4.0	2.9	2.9
60	15.5	19.6	6.5	7.4
90	33.0	63.3	22.5	26.3
110	57.6	140.0	37.5	65.9
Clarity	Poor	Fair	Excellent	Excellent

Example #2

Five stabilized flexible PVC resin formulations (two Prior Art, i.e., compositions X and Y as well as three of the instant invention, i.e., compositions D, E and F) were made in accordance with the components and quantities thereof as shown in Table V.

Table V

Component	Parts
PVC Resin	100
Plasticizer	35
Epoxidized soybean oil	3
CaCO ₃	20
Stearic Acid	0.2
Stabilizing blend	2.5

The Yellowness Index was measured for two prior art stabilizer additive packages in contrast to three compositions of the instant invention using the compositions of Table V in a short term static heat stability test. As is clearly seen in the following Table VI, the heat stability was not only equivalent to, but superior prior art formulations, but without additional heavy metals. Additionally, the volatility of the stabilizers was significantly less than that exhibited by Prior Art formulations, which is directly attributable to plate out, which increases with volatility as evidenced by the red to pink color of the clean out sheet, an undesirable feature for PVC sheets or films.

Table VI

Color (Yellowness Index) Value					
Time (min)	Prior Art X	Prior Art Y	D (72 ppm Zn)	E (180 ppm Zn)	F (180 ppm Zn)
0	1.7	2.4	1.8	1.5	1.6
15	2.7	2.6	2.4	1.7	2.6
60	19.4	16.9	11.2	12.1	16.1
105	28.4	26.8	20.7	20.1	20.3
165	Char	44.7	43.7	44.9	Char
% weight loss	20.1	12.3	1.1	0.6	0.2
Color of clean out sheet	Bright Red to Pink	Light Pink	White	White	White

Example #3

Two stabilized flexible PVC resin formulations (one Prior Art, i.e., composition U as well as one of the instant invention, i.e., composition A) were made in accordance with the components and quantities thereof as shown in Table VII.

Table VII

Component	<u>Parts</u>
PVC Resin	100
Impact Modifier	11
Epoxidized soybean oil	15
Processing Aid	3
Surfactant	3
Lubricant	1.0
Stabilizer	1.3

The Yellowness Index was measured for the prior art stabilizer additive package in contrast to a composition of the instant invention using the composition of Table VII in a short term static heat stability test. As is clearly seen in the following Table VIII, the dynamic and static heat stability were not only equivalent to, but superior to a Prior Art formulation, but without additional heavy metals.

Tabl VIII

C lor (Yellowness Index) Valu			C l r (Yellowness Index) Value		
	Prior Art U	A (120ppm)		Prior Art U	A (120ppm)
Time (min)	Dynamic Thermal Stability		Time (min)	Static Thermal Stability	
0	15	7	0	5.2	3.1
3	26	14	10	8.3	5.0
6	45	30	20	12.7	6.4
9	62	51	30	18.5	13.2
12	96	78	40	30.1	18.1
15	Char	char	50	39.4	29.8
18			60	52.1	46.7
			70	Char	72.1
			80		Char

Example #4

While levels of Zn in the range of 100-500 ppm are believed to be preferred, depending on the level of performance desired by the end-user, higher levels of Zn, e.g., 480 ppm can be added to the system, but still achieve acceptable performance.

Table IX

Component	Parts
PVC Resin	100
Plasticizer	41
Epoxidized soybean oil	3
CaCO ₃	40
Surfactant	3
ATH	5
Lubricants	0.25
Stabilizer	2

The Yellowness Index was measured for the Prior Art stabilizer additive package in contrast to a composition of the instant invention using the compositions of Table IX in a short term static heat stability test. As is clearly seen in the following Table X, the heat

stability was not only equivalent to, but superior prior art formulation, but without additional heavy metals. Additionally, the volatility of the stabilizers was significantly less than that exhibited by Prior Art formulations, which is directly attributable to plate out, which increases with volatility as evidenced by the red to pink color of the clean out sheet, an undesirable feature for PVC sheets or films.

Table X

Time (min)	Color (Yellowness Index) Value	
	Prior Art Z	G (480ppm)
0	8.9	6.1
20	9.5	7.3
60	15.8	12.1
110	30.7	28.9
% weight loss	36.1	0.9
Color of clean out sheet	Bright Red to Pink	White

Example #5

The impact of Zn level with any one particular class of phosphite ester is was compared by using the formulation illustrated in Table XI with various levels of zinc in various phosphite stabilizers shown in Table XII. The level of zinc was varied from 0 ppm to 400 ppm.

Table XI

Component	Parts
PVC Resin	100
Plasticizer	45
Epoxidized soybean oil	5
CaCO ₃	20
Stearic acid	0.25
Phosphite	2

Tabl XIII

Component	Parts
PVC Resin	100
Plasticizer	45
Epoxidized soybean oil	5
CaCO ₃	20
Stearic acid	0.25
Phosphite	various

Table XIV

Time (min)	Color (Yellowness Index) Value			
	Ba/Cd	Ba/Zn	Ba/Cd/Zn	B
0	1.4	1.2	1.6	1.5
30	1.7	1.5	2.2	1.7
75	8.9	9.9	8.3	5.8
120	12.7	16.7	10.8	9.9
150	15.7	21.9	15.1	14.4

Example #7

A stabilization for a pool liner composition was performed using the composition of Table XIII was formulated using 3.5 phr of stabilizer, the Yellowness Index results of which are shown in Table XV for several Prior Art additives..

Table XV

Time (min)	Color (Yellowness Index) Value			
	Ba/Cd	Ba/Zn	Ba/Cd/Zn	B
0	1.7	1.1	1.6	1.2
20	2.2	1.9	2.3	1.5
40	4.1	3.5	3.5	3.3
70	11.8	8.1	9.8	7.7
100	16.2	22.7	21.8	13.2
120	23.0	36.0	32.5	21.9

Example #10

While complete replacements of existing Prior Art additive packages are envisioned, there is no need to limit the invention to such. In fact, partial replacements are within the scope of the invention, such replacements ranging from 0.01% to 100% of the Prior Art additive.

Table XIX

Component	<u>Parts</u>
PVC Resin	100
Plasticizer	55
Epoxidized soybean oil	3
TiO ₂	7
Stearic acid	0.3
Stabilizer	3.5

Table XX

Time (min)	Color (Yellowness Index) Values	
	W	B (50%) replacement
0	1.1	0.8
20	1.9	1.7
40	2.5	2.3
80	13.4	10.4
100	22.7	14.9
120	Char	25.3

Example #11

The performance of a substituted bisphenolic phosphite ester, DOVERPHOS 479 was compared to other phosphite esters using the formulation illustrated in Table XXI with data as shown in Table XXII.

Table XXI

Component	Parts
PVC Resin	100
Plasticizer	38
Epoxidized soybean oil	3
Stearic acid	0.2
Zinc stearate (10% Zn by weight)	0.08
Phosphite	Various

Table XXII

Time	Color (Yellowness Index) Value				
	2 phr Doverphos® 4	2 phr Doverphos® 479	1 phr Doverphos® 479	0.4 phr Doverphos® 479	2 phr Doverphos® 53
Time (min) at 180°C					
0	1.8	2.5	1.5	1.5	0.9
20	2.5	2.9	2.0	1.9	1.2
50	4.4	4.5	3.1	3.0	3.3
80	56.6	9.4	7.6	16.5	12.1
110	89.1	13.4	19.0	Char	45.3
120	char	16.3	30.0		107
Time (hrs) at 80°C					
0	7.5	8.3	6.1	6.2	5.4
48	13.2	12.8	10.6	11.1	8.7
144	24.3	21.5	19.7	21.5	17.9
192	30	25.2	24.0	26.0	24.8
240	35.5	29.0	28.0	30.6	31.3
336	47.4	35.9	35.3	38.8	42.7
408	56.0	41.1	40.5	45.0	47.1
480	64.2	46.2	45.4	50.7	50.5
Time (hrs) using Xenon Arc Weatherometer (63°C)					
0	7.5	8.3	6.1	6.2	5.4
24	12.8	9.7	6.4	6.2	5.6